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(54) Title: SUCCINIC ACID DERIVATIVE DEGRADABLE CHELANTS, USES AND COMPOSITIONS THEREOF		
(57) Abstract <p>Polyamino disuccinic acids are effective chelants for use in photography and gas conditioning (both applications preferably involving the polyamino disuccinic acid in the form of a metal, preferably an iron complex). The copper chelates are also useful in electroless copper plating. In photography, the invention includes a method of bleaching or bleach-fixing a photographic material which comprises contacting said material with a bleaching solution containing a bleaching agent comprising a ferric complex of a polyamino disuccinic acid and the solution so used. In electroless deposition, the invention includes a method of electroless deposition of copper upon a non-metallic surface receptive to the deposited copper including a step of contacting the non-metallic surface with an aqueous solution comprising a soluble copper salt and a polyamino disuccinic acid and plating baths appropriate for such use. Another aspect of the invention includes a method for removing iron oxide deposits from a surface including a step of contacting the deposits with a solution comprising an ammoniated polyamino disuccinic acid. Yet another aspect of the invention involves gas conditioning including a process of removing H₂S from a fluid comprising contacting said fluid with an aqueous solution at a pH suitable for removing H₂S wherein said solution contains at least one higher valence polyvalent metal chelate of a polyamino disuccinic acid and a process of removing NO_x from a fluid comprising contacting the fluid with an aqueous solution of at least one lower valence state polyvalent metal chelate of a polyamino disuccinic acid.</p>		

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SUCCINIC ACID DERIVATIVE DEGRADABLE CHELANTS, USES AND COMPOSITIONS THEREOF

This invention relates to chelants, particularly uses of certain degradable
5 chelants.

Chelants or chelating agents are compounds which form coordinate
covalent bonds with a metal ion to form chelates. Chelates are coordination
compounds in which a central metal atom is bonded to two or more other
10 atoms in at least one other molecule or ion (called ligand) such that at least
one heterocyclic ring is formed with the metal atom as part of each ring.

Chelants are used in a variety of applications including food processing,
soaps, detergents, cleaning products, personal care products,
15 pharmaceuticals, pulp and paper processing, water treatment, metalworking
and metal plating solutions, textile processing solutions, fertilizers, animal
feeds, herbicides, rubber and polymer chemistry, photofinishing, and oil field
chemistry. Some of these activities result in chelants entering the
environment. For instance, agricultural uses or detergent uses may result in
20 measurable quantities of the chelants being in water. It is, therefore, desirable
that chelants degrade after use.

Biodegradability, that is susceptibility to degradation by microbes, is
particularly useful because the microbes are generally naturally present in
25 environments into which the chelants may be introduced. Commonly used
chelants like EDTA (ethylenediamine tetraacetic acid) are biodegradable, but
at rates somewhat slower and under conditions considered by some to be less
than optimum. (See, Tiedje, "Microbial Degradation of
Ethylenediaminetetraacetate in Soils and Sediments," Applied Microbiology,
30 Aug. 1975, pp. 327-329.) It would be desirable to have a chelating agent
which degrades faster than EDTA or other commonly used chelants.

While degradation of the chelant compounds themselves is an important
factor in ascertaining their fate in the environment, it is also important to
35 consider the form(s) in which the compound is likely to be found in a natural
environment like a lake, river or soil. In contact with such environments,
chelants can frequently be expected to be in the form of their chelates with

metals present in the environment or metals acquired in use of the chelant. The specific metal chelated depends on the metals present, their relative concentrations and availability, and the relative affinity (e.g. as expressed by stability constants which can be calculated by comparing potentiometric pH measurement of the chelant in the absence of and in the presence of known concentrations of metal ion as described in DETERMINATION AND USE OF STABILITY CONSTANTS by Martell and Motekaitis, VCH Publishers, 1985, pp. 14 and 21-27.) of the chelant for each metal present. It is often important that the chelant degrade well in the form of its iron, copper, manganese or calcium complexes. It would be desirable for a chelant compound to degrade in the form(s) it is most likely to be found in the environment. This form is commonly the iron complex. (See, Laurent et al., IVL Report, "Effect of Complex Formers on the Aquatic Environment, NTA, EDTA and DTPA", Inst. Water and Air Conservation Research (IVL), Stockholm, Pub. B921, Dec. 1988.

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Some chelants are at least somewhat biodegradable, but have other disadvantages that reduce their suitability for applications that may result in their presence in water.

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Polyamino disuccinic acids have been recognized as having some chelating properties but have not received wide usage. For instance, a better known member of the family, namely ethylenediamine disuccinic acid (EDDS), has not been widely used because it has less ability to chelate certain metal ions such as calcium and magnesium than more widely used chelants. The preparation of polyamino disuccinic acids is discussed by Kezerian et al. in U.S. Patent 3,158,635 where their use in rust removal is disclosed. Atkinson in U.S. Patent 4,704,233 disclose use of EDDS in detergents to enhance removal of organic stains and mention its biodegradability.

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Biodegradation is of particular interest in photography, but finding a commercially useful biodegradable chelant has been difficult. Chelates are particularly useful in the photographic industry as iron complexes used as oxidizing agents, commonly referred to as bleaching agents, for removing silver halide images. However, the chelating agents that are most useful do not biodegrade in a desirable time (e.g. ethylenediaminetetraacetic acid, N-hydroxyethylethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid,

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cyclohexanediaminetetraacetic acid, and propylenediaminetetraacetic acid all biodegrade less than 80% in 28 days using the semicontinuous activated sludge test.

5 Chelating ability is not indicative of redox ability of chelates of metal ions capable of more than one valence state. Nor can redox ability be predicted from structure as explained by R. Wichmann et al in "A New Bleaching Agent," presented at Imaging Science and Technology's 7th International Symposium on Photofinishing Technology, and published in R. Wichmann et al. "Advance
10 Printing of Paper Summaries; Seventh International Symposium on Photofinishing Technology," Las Vegas, NV, February 3-5, 1992 pp. 12-14.

It would be desirable to have a chelant useful in photographic processes and in other redox applications, particularly as a bleaching agent in
15 photography, which chelant is greater than 80 percent biodegradable within less than 28 days according to the semicontinuous activated sludge test (ASTM D-2667-82).

In this invention the ferric chelates of polyamino disuccinic acids
20 such as EDDS have been found to be excellent oxidizing agents for use in photographic bleach, bleach-fixing solutions for the bleaching of photographic silver.

In one aspect, the invention includes a method of bleaching or
25 bleach-fixing a photographic material which comprises contacting said material with a bleaching solution containing a bleaching agent comprising a ferric complex of a polyamino disuccinic acid. This invention includes the use of a ferric complex of a polyamino disuccinic acid in bleaching or bleach-fixing a photographic material. Additionally, the
30 invention includes an aqueous photographic bleaching solution comprising a water-soluble halide and as the bleaching agent a ferric complex of a polyamino disuccinic acid.

The invention also includes methods of electroless plating using
35 various metals, especially copper. It includes a method of electroless deposition of copper upon a non-metallic surface receptive to the deposited copper characterized in that the non-metallic surface is

contacted with an aqueous solution comprising a soluble copper salt and a polyamino disuccinic acid. Also included is a method of electroless copper plating which comprises immersing a receptive surface to be plated in an alkaline, autocatalytic copper bath comprising water, a water soluble copper salt, and a polyamino disuccinic acid complexing agent for cupric ion. Additionally, there is an improvement in a process for plating copper on non-metallic surfaces, only selected portions of which have been pretreated for the reception of electroless copper, by immersing the surface in an autocatalytic alkaline aqueous solution comprising, in proportions capable of effecting electroless deposition of copper, a water soluble copper salt, a complexing agent for cupric ion, and a reducing agent for cupric ion, the improvement comprising using as the complexing agent for cupric ion, a polyamino disuccinic acid. The invention includes a bath for the electroless plating of copper characterized in that, a polyamino disuccinic acid is used as complexing agent for cupric ions.

Another aspect of the invention includes a method for removing iron oxide deposits from a surface characterized in that the deposits are contacted with a solution comprising an ammoniated polyamino disuccinic acid.

Yet another aspect of the invention involves gas conditioning. In this aspect the invention includes a method of removing H_2S from a fluid comprising contacting said fluid with an aqueous solution at a pH suitable for removing H_2S characterized in that said solution contains at least one higher valence polyvalent metal chelate of a polyamino disuccinic acid. Another aspect of the gas conditioning invention includes a method of removing NO_x from a fluid characterized in that the fluid is contacted with an aqueous solution of at least one lower valence state polyvalent metal chelate of a polyamino disuccinic acid.

Polyamino disuccinic acids are compounds having at least two amine groups to of at least two of which is attached a succinic acid (or salt) group, preferably only two nitrogen atoms each have one succinic acid (or salt) group attached thereto. That is, the compounds have at least two nitrogen atoms to which a succinic acid or salt group is attached and may optionally have additional nitrogen atoms with or without succinic groups. The compound has at least 2 nitrogen atoms, and due to the commercial availability of the amine,

preferably has no more than 10 nitrogen atoms, more preferably no more than 6, most preferably 2 nitrogen atoms. Preferably no more than 4 nitrogen atoms, more preferably no more than 3, most preferably 2 nitrogen atoms are substituted with succinic acid groups. Remaining nitrogen atoms most
5 preferably are substituted with hydrogen atoms. More preferably, the succinic acid groups are on terminal nitrogen atoms, most preferably each of which nitrogens also has a hydrogen substituent. Because of steric hindrance of two succinic groups on one nitrogen, it is preferred that each nitrogen having a succinic group has only one such group. Remaining bonds on nitrogens
10 having a succinic acid group are preferably filled by hydrogens or alkyl or alkylene groups (linear, branched or cyclic including cyclic structures joining more than one nitrogen atom or more than one bond of a single nitrogen atom, preferably linear) or such groups having ether or thioether linkages, all of preferably from 1 to 10 carbon atoms, more preferably from 1 to 6, most
15 preferably from 1 to 3 carbon atoms, but most preferably hydrogen. More preferably, the nitrogen atoms are linked by alkylene groups, preferably each of from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, even more preferably from 2 to 8, most preferably from 2 to 6 carbon atoms. The polyamino disuccinic acid compound preferably has at least 10 carbon
20 atoms and preferably has at most 50, more preferably at most 40, most preferably at most 30 carbon atoms. The term "succinic acid" is used herein for the acid and salts thereof; the salts include metal cation (e.g. potassium, sodium) and ammonium or amine salts. Polyamino disuccinic acids useful in the practice of the invention are unsubstituted (preferably) or inertly
25 substituted, that is substituted with groups that do not undesirably interfere with the activity of the polyamino disuccinic acid in a selected application, particularly photographic uses. Such inert substituents include but are not limited to alkyl groups (preferably of from 1 to 6 carbon atoms); and aryl groups including arylalkyl and alkylaryl groups (preferably of from 6 to 12 carbon
30 atoms), with alkyl groups preferred among these and methyl and ethyl groups preferred among alkyl groups. Inert substituents are suitably on any portion of the molecule, preferably on carbon atoms, more preferably on alkylene groups, for example alkylene groups between nitrogen atoms or between carboxylic acid groups, most preferably on alkylene groups between nitrogen groups.

Preferred polyamino disuccinic acids include ethylenediamine N,N'-disuccinic acid, diethylenetriamine N,N"-disuccinic acid, triethylenetetraamine N,N""-disuccinic acid, 1,6-hexamethylenediamine N,N'-disuccinic acid, tetraethylenepentamine N,N""-disuccinic acid, 2-hydroxypropylene-1,3-diamine N,N'-disuccinic acid, 1,2-propylenediamine N, N'-disuccinic acid, 1,3-propylenediamine N,N'-disuccinic acid, cis-cyclohexanediamine N,N'-disuccinic acid, trans-cyclohexanediamine N,N'-disuccinic acid, and ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid.

Such polyamino disuccinic acids can be prepared, for instance, by the process disclosed by Kezerian et al. in U.S. Patent 3,158,635 which is incorporated herein by reference in its entirety. Kezerian et al disclose reacting maleic anhydride (or ester or salt) with a polyamine corresponding to the desired polyamino disuccinic acid under alkaline conditions. The reaction yields a number of optical isomers, for example, the reaction of ethylenediamine with maleic anhydride yields a mixture of three optical isomers [R,R], [S,S] and [S,R] ethylenediamine disuccinic acid (EDDS) because there are two asymmetric carbon atoms in ethylenediamine disuccinic acid. These mixtures are used as mixtures or alternatively separated by means within the state of the art to obtain the desired isomer(s). Alternatively, [S,S] isomers are prepared by reaction of such acids as L-aspartic acid with such compounds as 1,2-dibromoethane as described by Neal and Rose, "Stereospecific Ligands and Their Complexes of Ethylenediaminedisuccinic Acid", Inorganic Chemistry, v. 7. (1968), pp. 2405-2412.

The invention includes use of iron complexes of polyamino disuccinic acids such as ethylenediamine disuccinic acid (EDDS), especially in photography. The ferric complexes are also useful in abatement of hydrogen sulfide and other acid gases and as a source of iron in plant nutrition. Similarly other metal complexes such as the copper, zinc and manganese complexes supply those trace metals in plant nutrition. The ferrous complexes are useful in nitrogen oxide abatement.

Iron complexes of polyamino disuccinic acid are conveniently formed by mixing an iron compound with an aqueous solution of the polyamino disuccinic acid (or salt). The pH of the resulting iron chelate solution is preferably

adjusted with an alkaline material such as ammonia solution, sodium carbonate, or dilute caustic (NaOH). Water soluble iron compounds are conveniently used. Exemplary iron compounds include iron nitrate, iron sulfate, and iron chloride. The final pH of the iron chelate solution is preferably
5 in the range of 4 to 9, more preferably in the range of 5 to 8. When an insoluble iron source is used, such as iron oxide, then the polyamino disuccinic acid is preferably heated with the iron oxide in an aqueous medium at an acidic pH. The use of an ammoniated polyamino disuccinic acid solution is particularly effective. Ammoniated polyamino disuccinic acid chelants are
10 conveniently formed by combining ammonium or aqueous ammonia solutions and aqueous solutions or slurries of polyamino disuccinic acids in the acid (rather than salt) form.

Polyamino disuccinic acids are effective as chelants especially for
15 metals such as iron and copper. Effectiveness as a chelant is conveniently measured by complexing the chelant with a metal such as copper such as by mixing an aqueous solution of known concentration of the chelant with an aqueous solution containing copper (II) ions of known concentration and measuring chelation capacity by titrating the chelant with copper in the
20 presence of an indicator dye, using as an endpoint detector a photosensitive electrode.

Chelating capacity is not, however, a direct indicator of effectiveness in activities such as bleach fixing solutions for photography. For instance, N-methyliminodiacetic acid (MIDA) is a relatively poor chelating agent for ferric
25 iron, requiring 2 to 3 moles of chelant to complex and solublize one mole of iron. The ferric complex of MIDA, however, is a strong bleaching agent.

Ethylenediamine disuccinic acid is biodegradable using a standardized
30 test such as ASTM D-2667-82. In that test, a standardized sludge containing municipal waste treatment plant organisms is used to biodegrade the chelant in the presence of metal ions representative of those found in the environment including iron. Such a test simulates the environment encountered in a municipal waste treatment plant for screening the inherent biodegradability of
35 non-volatile, water-soluble compounds. EDDS in this test was found to be greater than 80 percent biodegradable in less than 28 days.

Polyamino disuccinic acids are preferably employed in the form of water-soluble salts, notably alkali metal salts, ammonium salts, or alkyl ammonium salts. The alkali metal salts can involve one or a mixture of alkali metal salts although the potassium or sodium salts, especially the partial or complete sodium salts of the acids are preferred because of their relatively low cost and enhanced effectiveness.

Polyamino disuccinic acids are particularly useful in photography, especially as a bleaching agent in bleach fixing solutions in the form of their iron (III) complexes. The solutions are used to bleach a photographic material preferably having at least one silver halide layer or component.

Polyamino disuccinic acids used as bleaching agents which are components of the bleaching compositions and bleach-fixing compositions of this invention are preferably utilized in the form of water-soluble salts, such as ammonium or alkali metal salts, of a ferric polyamino disuccinic acid complex. Alternatively, the ferric complex of the present invention is used as free acid (hydrogen), alkali metal salt such as sodium salt, potassium salt, lithium salt, or ammonium salt, or a water soluble amine salt such as triethanolamine salt. Preferably, the potassium salt, sodium salt or ammonium salt is used. It is optional to use the ferric complex in combination with one more aminopolycarboxylic compounds.

The amount of polyamino disuccinic acid to be used depends on the amount of silver and the silver halide composition in the light-sensitive material to be processed. It is preferred to employ 0.01 mole or more, more preferably 0.05 to 1.0 mole, per liter of solution employed; preferably there is a molar ratio of polyamino disuccinic acid to ferric ion of from 1:1 to 5:1. In a supplemental solution, for supplying a smaller amount of more concentrated solution, the solution is conveniently employed at the maximum concentration permitted by the solubility of the polyamino disuccinic acid compound. The bleach compositions of this invention preferably contain 5 to 400 grams per liter of the polyamino disuccinic acid bleaching agent, more preferably 10 to 200 grams per liter.

The bleach-fixing solution of the present invention is preferably used in a pH range of 2.0 to 10.0, more preferably 3.0 to 9.5, most preferably 4.0 to 9.0. The temperature for processing is conveniently 80° C or lower, more desirably 55° C or lower, for the purpose of suppressing evaporation. The bleach-fixing processing time is preferably within 8 minutes, more preferably with 6 minutes.

The bleach or bleach-fix compositions optionally contain other additives within the skill in the art, such as amines, sulfites, mercaptotriazoles, alkali metal bromides, alkali metal iodides, thiols and the like. An additional silver halide solvent such as water-soluble thiocyanate or potassium thiocyanate is optionally included in the bleach-fix compositions. The bleach-fix composition optionally also contains a non-chelated salt of an aminopolycarboxylic acid, e.g., sodium salts of EDDS acid, in addition to the ferric salt.

As additives which can contribute to bleach-fixing characteristics, it is desirable to include alkali metal halides or ammonium halides, such as potassium bromide, sodium bromide, sodium chloride, ammonium bromide, ammonium iodide, sodium iodide, potassium iodide, and the like. Other optional additives include solublizing agents such as triethanolamine, within the skill in the art for use in bleaching solutions such as acetylacetone, phosphonocarboxylic acid, polyphosphoric acid, organic phosphonic acid, oxycarboxylic acid, polycarboxylic acid, alkylamines, polyethyleneoxides, and the like.

Use of special bleach-fixing solutions such as a bleach fixing solution comprising a composition in which a halide such as potassium bromide is added in a small amount, or alternatively a bleach-fixing solution in which a halide such as potassium bromide, ammonium bromide and/or ammonium iodide, or potassium iodide is added in a large amount, and, in addition, a bleach-fixing solution with a composition comprising a combination of the bleaching agent of the present invention and a large amount of a halide such as potassium bromide is within the scope of the invention.

Silver halide fixing agents suitable for incorporation in the bleach-fixing solutions of the present invention are preferably compounds within the skill in

the art for fixing processing which can react with a silver halide to form a water soluble complex, and include thiosulfates such as potassium thiosulfate, sodium thiosulfate, and ammonium thiosulfate; thiocyanates such as potassium thiocyanate, sodium thiocyanate, ammonium thiocyanate, thiourea, thioether; highly concentrated bromides and iodides. These fixing agents are conveniently used in amounts within the range which can be dissolved, namely 5 g/liter or more, preferably 50 g/liter or more, more preferably 70 g/liter or more; more preferably there are less than 400, most preferably less than 200 grams per liter.

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The bleach-fixing solution of the present invention optionally also contains various pH buffers such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, acetic acid, sodium acetate, and ammonium hydroxide, either singly or in a combination of two or more compounds. Optional ingredients include various fluorescent whitening agents, defoaming agents, antifungal agents, preservatives such as hydroxylamine, hydrazine, sulfites, metabisulfites, bisulfite adducts of aldehyde or ketone compounds, or other additives. Organic solvents such as methanol, dimethylformamide, and dimethyl sulfoxide are optionally included. Addition of a polymer or a copolymer having a vinyl pyrrolidone nucleus as disclosed in Japanese Provisional Patent Publication No. 10303/1985 is also within the scope of the invention.

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Other optional compounds in the bleach-fixing solution of the present invention for accelerating bleach-fixing characteristics, include tetramethylurea, phosphoric trisdimethylamide, ϵ -caprolactam, N-methylpyrrolidone, N-methylmorpholine, tetraethyleneglycol monophenyl ether, acetonitrile, and glycol monomethyl ether.

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In the photographic processing method of the present invention, it is preferred that the bleach-fixing step of the present invention is performed immediately after color developing, but optionally, alternatively, following processing such as water washing, or rising or stopping after color developing. Most preferably the bleach-fixing processing of the present invention is conducted, after pre-fixing processing after color developing.

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Bleach-fixing processing is optionally followed by stabilizing the processing with or without washing with water before or after stabilizing processing. In addition to the listed steps, there are optionally various auxiliary steps such as steps of film hardening, neutralization, black-and-white developing, reversal, and washings with a small amount of water, if desired. Typical examples of preferable processing methods may include the various steps as shown below:

- 10 (1) Color developing→Bleach-fixing→Water washing
- (2) Color developing→Bleach-fixing→Washing with a small amount of water→Water washing
- (3) Color developing→Bleach-fixing→Water washing→Stabilizing
- (4) Color developing→Bleach-fixing→Stabilizing
- 15 (5) Color developing→Bleach-fixing→First Stabilizing→Second Stabilizing
- (6) Color developing→Water washing (or stabilizing)→Bleach-fixing→Water washing (or stabilizing)
- (7) Color developing→Pre-fixing→Bleach-fixing→Water washing
- (8) Color developing→Pre-fixing→Bleach-fixing→Stabilizing
- 20 (9) Color developing→Pre-fixing→Bleach-fixing→First stabilizing→Second stabilizing
- (10) Color developing→Stopping→Bleach-fixing→Water washing→Stabilizing.

25 Of these processing steps, those of (3), (4), (5), (8) and (9) are preferably employed in the present invention, with processing steps of (4), (5), (8) and (9) most preferred.

30 In the bleach-fixing solution of the present invention, chelating agents and/or ferric complexes thereof outside the scope of the present invention are optionally added. However, it is preferred to use the ferric complex outside the scope of the present invention at a proportion of 0.45 mole percent or less relative to the organic acid ferric complexes of the present invention.

35 The reduced product of the iron complex formed in use of the bleach-fixing solution is optionally returned to the oxidized state, preferably by an

oxidation treatment. Oxidation treatments include, for instance, introducing air or oxygen bubbles for example into the processing solution in the bleaching solution tank or the bleach-fixing solution tank, e.g., in an automatic developing machine, or by natural contact of the air on the liquid surface. For oxidation, effective contact of air or oxygen and solution is needed. Such contact is within the skill in the art and achieved by such means as stirring.

Polyamino disuccinic acids are also useful, for instance, in food products vulnerable to metal-catalyzed spoilage or discoloration; in cleaning products for removing metal ions, that may reduce the effectiveness, appearance, stability, rinsibility, bleaching effectiveness, germicidal effectiveness or other property of the cleaning agents; in personal care products like creams, lotions, deodorants and ointments to avoid deleterious effects such as metal-catalyzed oxidation, rancidity, turbidity, and reduced shelf-life; in pulp and paper processing to enhance or maintain bleaching effectiveness; in pipes, vessels, heat exchangers, evaporators, filters and other equipment to avoid or remove scaling, in pharmaceuticals; in metal working; in textile preparation, desizing, scouring, bleaching, dyeing; in agriculture as in chelated micronutrients or herbicides; in polymerization or stabilization of polymers; in the oil field such as for drilling, production, recovery, hydrogen sulfide abatement.

The chelants can be used in industrial processes whenever metal ions such as iron or copper are a nuisance and are to be prevented.

The polyamine disuccinic acids are also useful in processes for the electroless deposition of metals such as nickel and copper. Electroless plating is the controlled autocatalytic deposition of a continuous film of metal without the assistance of an external supply of electrons such as described in U.S. Patents 3,119,709 (Atkinson) and 3,257,215 (Schneble et al.). Non-metallic surfaces are pretreated by means within the skill in the art to make them receptive or autocatalytic for deposition. All or selected portions of a surface are suitably pretreated. Complexing agents are used to chelate a metal being deposited and prevent the metal from being precipitated from solution (that is as the hydroxide). Chelating a metal renders the metal available to the reducing agent which converts the metal ions to metallic form. Growth of electroless plating can be attributed in part to growth of the electronics

industry, especially for printed circuits. Electroless plating solutions are complex and contain a variety of ingredients. For example, an illustrative electroless copper solution would advantageously contain copper salts, a reducing agent, a material for the adjustment of the pH, a complexing agent, a buffer, and various additives to control qualities such as stability, film properties, deposition rates. Typical copper salts include the water soluble salts such as copper sulfate, chloride, nitrate and acetate. Other organic and inorganic salts of copper may also be used. Typical of the reducing agents that can be used in alkaline electroless copper plating baths are formaldehyde and formaldehyde precursors such as glyoxal and paraformaldehyde. Borohydrides such as sodium or potassium borohydride and boranes such as amino boranes are also useful. In acidic copper solutions, hypophosphites such as sodium or potassium hypophosphite are used. On the acidic side, acids such as sulfuric may be employed. The pH adjustment is used to regulate the plating potential of the bath. A polyamino disuccinic acid is preferably used to chelate the copper. A typical aqueous bath utilizing the polyamino disuccinic acids advantageously contains from 0.002 to 0.60 moles of a water soluble copper salt, the polyamino disuccinic acid at a molar ratio of approximately 1 to 2 times that required to complex the copper, an alkali metal hydroxide in sufficient amounts to give a pH of from 10 to 14, and for example formaldehyde from 0.03 to 1.3 moles per liter. One particularly important need in the electroless metal plating baths are for chemicals of high purity. This can be extremely important since the surfaces being plated must be autocatalytically active. Many impurities poison the catalytic surface even when present in very small amounts. When this is the case, it is important that the chelating agents that are used be of high purity. Polyamino disuccinic acids that are especially effective and lend themselves to being easily purified by isolation as the water insoluble acid form include ethylenediamine disuccinic acid, diethylenetriamine disuccinic acid, and hexamethylenediamine disuccinic acid. Ethylenediamine disuccinic acid is a particularly preferred chelant. Used plating solutions, especially copper plating solutions, may be difficult to treat since they contain strong complexes such as EDTA (ethylenediaminetetraacetic acid) that are slowly biodegraded. The use of more biodegradable chelants such as EDDS are particularly useful in this regard.

In the polymerization of rubber polyamino disuccinic acids are suitably used for preparing for example the redox catalysts used therein. They additionally prevent the precipitation of such compounds as iron hydroxide in an alkaline polymerization medium.

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In the textile industry, the chelants are suitably used for removing metal traces during the manufacture and dyeing of natural and synthetic fibers, thereby preventing many problems, such as dirt spots and stripes on the textile material, loss of luster, poor wettability, unlevelness and off-shade dyeings.

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Exemplary of various other uses are applications in pharmaceuticals, cosmetics and foodstuffs where metal catalyzed oxidation of olefinic double bonds and hence rancidification of goods is prevented. The chelates are also useful as catalysts for organic syntheses (for example air oxidation of paraffins, hydroformylation of olefins to alcohols).

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Metal chelates are important in agriculture because they supply micronutrients (trace metals such as iron, zinc, manganese, and copper) which are vital in the metabolism of both plants and animals. Plant problems previously ascribed to disease and drought are now recognized as possible symptoms of micronutrient deficiencies. Today these deficiencies are generally considered to be caused by (1) the trend toward higher analysis fertilizers containing fewer "impurities"; soils which had been adequately supplied with trace metals from these "impurities" have now become deficient (2) intensified cropping practices which place a severe demand on the soil to supply micronutrients; to maintain high yields, supplementary addition of trace metals is now necessary (3) high phosphorus fertilization, which tends to tie up metals in the soil in a form unavailable to the plant and (4) the leveling of marginal land for cultivation, which often exposes subsoils deficient in micronutrients. The metal chelates of aminocarboxylates such as EDTA and HEDTA are commonly used to chelate micronutrients for agricultural use. The iron, copper, zinc, and manganese chelates of the polyamino disuccinic acids such as EDDS can be used to deliver these metals to the plant. Because of the excellent solubility, these metal chelates are more readily utilized by the plant than are the inorganic forms of the metals. This is especially true in highly competitive ionic systems. As a result, the micronutrients that are

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chelated to the polyamino disuccinic acids are more efficient than when compared to the inorganic sources. The iron chelates of iron, manganese, copper, and zinc with the biodegradable polyamino disuccinic acid EDDS are particularly preferred. Biodegradable chelants would have less residence time in soil.

Further fields of application for polyamino disuccinic acids include gas washing, conditioning or scrubbing (of for example flue, geothermal, sour, synthesis, process, fuel, or hydrocarbon gas) to remove at least one acidic gas, preferably the removal of NO_x from flue gases, H_2S oxidation and metal extraction. Polyvalent metal chelates of polyamino disuccinic acids are particularly useful in removing H_2S from a fluid, particularly a gas, containing H_2S , by (directly or indirectly) contacting the fluid with at least one chelate of at least one, preferably one polyvalent metal in a higher valence state such that sulfur is formed along with the chelate of the metal in a lower valence state. The chelate of any oxidizing polyvalent metal capable of being reduced by reaction with H_2S or hydrosulfide and/or sulfide ions and, preferably which can be regenerated by oxidation, is suitable. Preferably the chelates are water soluble. Exemplary metals include lead, mercury, nickel, chromium, cobalt, tungsten, tin, vanadium, titanium, tantalum, platinum, palladium, zirconium, molybdenum, preferably iron, copper, or manganese, most preferably iron.

Polyamino disuccinic acids are suitably used in any process of removal of H_2S within the skill in the art such as those exemplified by United States Patents 4,421,733; 4,614,644; 4,629,608; 4,683,076; 4,696,802; 4,774,071; 4,816,238; and 4,830,838, which are incorporated by reference herein. The polyvalent metal chelates are readily formed in aqueous solution by reaction of an appropriate salt, oxide or hydroxide of the polyvalent metal and the chelating agent in the acid form or an alkali metal or ammonium salt thereof.

Preferably contact of H_2S , hydrosulfide, and/or sulfide with the chelate takes place at a pH of from 6 to 10. The more preferred range is from 6.5 to 9 and the most preferred range of pH is from 7 to 9. In general, operation at the highest portion of the range is preferred in order to operate at a high efficiency of hydrogen sulfide absorption. Since the hydrogen sulfide is an acid gas, there is a tendency for the hydrogen sulfide to lower the pH of the aqueous

alkaline solution. Lower pH is preferable in the presence of carbon dioxide to reduce absorption thereof. Optimum pH also depends upon stability of a particular polyvalent metal chelate. At the pH values below 6 the efficiency of hydrogen sulfide absorption is so low so as to be generally impractical. At pH values greater than 10, for instance with iron as the polyvalent metal, the precipitation of insoluble iron hydroxide may occur resulting in decomposition of the iron chelate. Those skilled in the art can ascertain a preferred pH for each operating situation.

Buffering agents optionally useful as components of aqueous alkaline scrubbing solutions of the invention include those which are capable of maintaining the aqueous alkaline solution at a pH generally in a operating pH range of 6 to 10. The buffering agents are advantageously water soluble at the concentration in which they are effective. Examples of suitable buffering agents include the ammonium or alkali metal salts of carbonates, bicarbonates, or borates, including sodium carbonate, bicarbonate or sodium borate, particularly carbonates and bicarbonates when used in the presence of CO₂ (carbon dioxide).

The temperatures employed in a contacting or absorption-contact zone are not generally critical, except that the reaction is carried out below the melting point of sulfur. In many commercial applications, absorption at ambient temperatures is desired. In general, temperatures from 10°C to 80°C are suitable, and temperatures from 20°C to 45°C are preferred. Contact times conveniently range from 1 second to 270 seconds or longer, with contact times of 2 seconds to 120 seconds being preferred.

Suitable pressure conditions vary widely, depending on the pressure of the gas to be treated. For example, pressures in a contacting zone may vary from one atmosphere up to one hundred fifty or even two hundred atmospheres, with from one atmosphere to one hundred atmospheres preferred.

In H₂S removal, preferably at least an amount of chelate in a higher valence state stoichiometric with the H₂S to be removed is used. Preferred mole ratios of chelate to H₂S are from 1:1 to 15:1, more preferably from 2:1 to

5:1. When chelates in both higher and lower valence states are present, it is generally preferable to maintain a concentration of lower valence state chelate at least 5 times the concentration of that in the higher valence state. When, for instance an iron chelate is used, it is preferably present in an amount from 100 to 100,000 ppm iron in the higher valence state most preferably from 1000 to 50,000 ppm by weight iron in the higher valence state. The circulation rate of the chelate solution depends upon the hydrogen sulfide level in the H₂S containing fluid. In general, the circulation rate should be sufficient to provide from 1 to 6 moles and preferably 2-4 moles of high valence (e.g. ferric) chelate for every mole of H₂S entering the reaction zone. The contact time of the reactants should be at least 0.05 second or more and preferably in the range from 0.02 to 1.0 seconds.

Polyamino disuccinic acids are preferably used in combination with additives such as rate enhancers (or catalysts, for example for conversion of H₂S to sulfur) and/or stabilizers for the chelates. Cationic polymeric catalysts are advantageous and include polyethyleamines, poly(2-hydroxypropyl-1-N-methylammonium chloride) and the 1,1-dimethyl analogue, poly[N-(dimethylaminomethyl) acrylamide], poly(2-vinylimidazolium bisulfate), poly(diallyldimethyl ammonium chloride) and poly(N-dimethyl aminopropyl)-methacrylamide. These cationic polymers are well known and are commercially available under various tradenames. See, for example, Commercial Organic Flocculants by J. Vostreil et al Noyes Data Corp. 1972 which is incorporated by reference herein. Other useful cationic catalysts are set forth in J. Macromol. Science-Chem. A4 pages 1327-1417 (1970) which is also incorporated by reference herein. Preferred catalysts include polyethylene amines and poly (diallyldimethyl ammonium chloride). Preferred concentration ranges for the polymeric catalysts are from 0.75 to 5.0 weight percent, and from 1.0 to 3.0 weight percent is the most preferred range. The amount of polymeric catalyst is sufficient to provide a weight ratio of iron or other polyvalent metal in the range from 0.2 to 10:1. Concentrations of from 10 to 25 ppm in solution are preferred. Stabilizing agents include, for example bisulfite ions such as sodium, potassium, lithium, ammonium bisulfite and mixtures thereof. They are used in stabilizing amounts, that is amounts sufficient to reduce or inhibit rate of degradation of the chelate, preferably from

0.01 to 0.6 equivalents per liter of solution, more preferably from 0.05 to 0.3 equivalents/liter.

After the chelate of lower valence state is produced from that of higher
5 valence state, it is preferably oxidized back to the higher valence state and recycled. Oxidation is suitably by any means within the skill in the art, for example electrochemically, but preferably by contact with an oxygen-containing gas, for example air. If CO_2 is absorbed, it is preferably removed before contact with the oxygen-containing gas. The oxygen (in
10 whatever form supplied) is advantageously supplied in a stoichiometric equivalent or excess with respect to the amount of lower valence state metal ion of the chelate or chelates present in the mixture. Preferably, the oxygen is supplied in an amount from 1.2 to 3 fold excess and in a concentration of from 1 percent to 100 percent by volume, more preferably from 5 percent to 25
15 percent by volume. Temperatures and pressures are suitably varied widely, but generally those used in the contacting zone(s) are preferred, preferably temperatures of from 10°C to 80°C more preferable from 20°C to 45°C with pressures from 0.5 atmosphere to 3 or 4 atmospheres preferred. Mild oxidizing conditions are generally preferred to avoid degradation of chelating
20 agent. Such conditions are within the skill in the art.

Sulfur produced by reaction of H_2S with the polyvalent metal chelate is optionally solubilized, for example by oxidation. Oxidation is suitably by any means within the skill in the art. When SO_2 is present or easily generated by
25 oxidation of H_2S (e.g. using oxygen or electrochemical means) it is a preferred oxidizing agent to produce, for example thiosulfates from the sulfur. Other suitable oxidizing agents include for example alkali metal or ammonium salts of inorganic oxidizing acids such as perchloric, chloric, hypochlorous, and permanganic acids. Otherwise, the sulfur is optionally recovered by means
30 within the skill in the art including flocculation, settling, centrifugation, filtration, flotation.

Processes of the invention include, for instance: a process for removing at least a portion of H_2S from a fluid stream containing H_2S which comprises
35 (A) contacting said fluid stream (optionally in a first reaction zone) with an aqueous solution at a pH range suitable for removing H_2S wherein said

solution comprises at least one higher valence polyvalent metal chelate of a polyamino disuccinic acid whereby said higher valence polyvalent metal chelate is reduced to a lower valence polyvalent metal chelate. Optionally the aqueous solution additionally comprises an oxidizing agent capable of
5 oxidizing elemental sulfur to soluble sulfur compounds, and/or one or more water soluble cationic polymeric catalysts and/or a stabilizing amount of a stabilizing agent each as bisulfite ion.

The process optionally includes at least one additional step such as:
10 (B) contacting said solution containing the lower valence polyvalent chelate in a second reaction zone with an oxygen-containing gas stream whereby said chelate is reoxidized;
(C) recirculating said reoxidized solution back to said first reaction zone;
(D) feeding said aqueous solution from said oxidation zone to a sulfur recovery
15 zone;
(E) removing from said aqueous solution at least a portion of said sulfur and thereafter;
(F) regenerating the aqueous admixture in a regeneration zone to produce a regenerated reactant;
20 (G) returning aqueous admixture containing regenerated reactant from the regeneration zone to the contacting zone;
(H) incinerating hydrogen sulfide to form sulfur dioxide;
(I) selectively absorbing said sulfur dioxide in an alkaline aqueous solution without substantial carbon dioxide absorption to form a solution of sulfites
25 essentially free of insoluble carbonates;
(J) contacting said sulfur with said sulfites to form soluble sulfur compounds;
(K) recirculating said reoxidized polyvalent metal chelate back to said fluid stream/aqueous chelate solution contacting step; and/or
(L) condensing geothermal steam in a reaction zone, preferably in said first
30 reaction zone, for contacting said reduced polyvalent metal chelate.

Compositions of the invention, thus, include aqueous solutions of polyvalent metal chelates of the invention (in one or more oxidation states) with at least one of: H_2S , sulfide or bisulfide ions, rate enhancers such as
35 poly(dimethyldiallyl ammonium chloride) and/or polyethylenamines, and/or stabilizers such as bisulfite ions.

Similarly, polyamino disuccinic acids are used in removal of nitrogen oxides, preferably nitric oxide (NO), from fluids containing them. For instance, nitrogen oxides (NO_x) and SO₂ can be removed from flue gas streams by absorbing the SO₂ using an absorbent or reactant therefor, particularly an amine based absorbent such as a nitrogen-containing heterocyclic compound preferably having at least one carbonyl group such as a piperazinone; piperidinone, piperidine, piperazine or triazine having a carbonyl group; hydantoin; cyclic urea, oxazolidone or morpholinone in conjunction with a chelate of a polyvalent metal. Representative metal ions are chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, palladium, platinum, tin, titanium, tungsten, and vanadium; preferably iron, copper, and/or nickel all preferably with a valence of +2, the more preferably iron, most preferably iron in the ferrous state. Such chelates are conveniently prepared by admixing a water soluble salt of the metal, such as a sulfate or acetate with a water soluble form of the chelating agent, for example a salt, advantageously in water. The chelates are useful in any process within the skill in the art such as those disclosed in United States Patents 4,732,744 to Chang et al.; 4,612,175 to Harkness et al.; 4,708,854 to Grinstead; 4,615,780 to Walker; 4,126,529 to DeBerry; 4,820,391 to Walker; and 4,957,716 to Cichanowicz et al. When an SO₂ absorbent is used, it is preferably regenerated, more preferably thermally regenerated, and preferably recycled. The concentration of NO_x in the fluid (directly or indirectly) contacting the chelate is preferably from 1 ppm to 15,000 ppm by volume such as is found, for instance, in flue gases from burning for example coal.

Whether used with an absorbent for SO₂ or not, the metal chelate is advantageously present in the solution which contacts the NO_x containing fluid at a metal ion concentration greater than 100 ppm with a chelating agent to metal ion molecular ratio of greater than or equal to one. The metal chelate is preferably present at a metal ion concentration of 1,000 to 10,000 ppm and a chelating agent to metal ion molecular ratio between 1:1 and 10:1. The optimum amounts depend on the chelating agent generally with preferred ratios between 1:1 and to 5:1.

An absorber is suitably operated at a temperature of from 0° to 120°C, but is preferably operated at a temperature of from 5° to 95°C. In the process, both absorber and (optionally) a stripper are typically operated at a pressure of from atmospheric to 10 atmospheres (e.g. 0 to 69 Pa gauge), however, atmospheric pressure is preferred for the convenience of lower equipment and operating costs and reduced SO₂ absorbent losses. Higher temperatures and pressures are not deleterious so long as they are below the decomposition temperature of the chelate and absorbent, if present. The absorber is preferably maintained at a pH between 3 and 8 to retain NO_x absorbance in the absorber.

Chelates absorb NO_x or act as stoichiometric reactants to increase the solubility of NO_x in aqueous solution. Preferably sulfite and/or bisulfite ions collectively referred to herein as "sulfites" are also present. Such ions react with the NO_x-chelate complex to form iminodisulfonate salts and free the chelate for NO_x absorption. Examples of suitable soluble sulfite salts include sodium, potassium, lithium, magnesium and/or ammonium sulfite and/or bisulfite. When SO₂ is present, SO₂ in aqueous solution forms sulfurous acid, and the concentration of sulfites in the absorbent is generally sufficient for iminodisulfonate formation without replenishment, but sulfites may be added, if necessary, to maintain a concentration of at least 0.05 to 1 g-moles/l absorbent, preferably at least 0.1 g-moles/l. A sulfite salt is, thus, preferably present with the chelate.

Alternatively, as described in U.S. Patent 4,957,716, which is incorporated herein by reference in its entirety, the chelate promotes absorption of NO_x which may be converted to such compounds as HNO₂ and HNO₃ which react with HSO₃, if present, to form hydroxylamine-disulfonate (HON(SO₃H)₂, abbreviated HADS) and related compounds, which are preferably subsequently converted to soluble ammonium and sulfate ions advantageously at a pH of 4.2 or less, preferably 4. More preferably the ammonium ions are subsequently removed, for example by absorption, and most preferably, the sulfate ions are precipitated.

In removing NO_x from a fluid, the polyvalent metal chelate is oxidized from a lower to a higher valence state. The lower valence metal chelate is

preferably replenished, for example by replacement of the polyvalent metal ion of the chelate, but more preferably by reduction of the metal by any means within the skill in the art, such as by contact with a reducing agent, or preferably by electrochemical means (at a cathode). The chelate is, then,
5 preferably recycled.

When electrochemical regeneration is used, the solution containing the higher valence polyvalent metal chelate (which solution is preferably first (advantageously thermally) stripped of SO_2) is preferably directed to a cathode
10 compartment of an electrochemical cell comprised of an anode in an anode compartment separated, preferably by a membrane, from a cathode in a cathode compartment. An electrical potential is imposed across the anode and cathode to reduce inactive oxidized chelates to an active state. Preferably, an anionic exchange membrane is used. Heat stable amine salts may also be
15 converted to free amine sorbent in the cathode compartment and soluble salt anions diffuse from the cathode compartment through the anion exchange membrane into the anode department. Preferably, in a further step, regenerated absorbent solution from the cathode compartment is recycled to the NO_x containing fluid contacting step. The process more preferably
20 additionally comprises a step of adjusting the pH of the regenerated recycle absorbent to from 3 to 8.

Compositions of the invention, thus, include aqueous solutions of the polyvalent metal polyamino disuccinic acids with at least one of NO_x , at least
25 one (water soluble) sulfite, or at least one absorbent for SO_2 . Mixtures of the chelates in higher and lower valence states and mixtures of the chelate with the chelate - NO_x complex are also aspects of the instant invention.

Processes of the invention, thus, include a process for removing at least
30 a portion of NO_x , preferably NO, from a fluid containing NO_x , said fluid preferably also containing SO_2 and said fluid preferably being a gas, but suitably being in a form such as a liquid, suspension, or condensate comprising the step of

35 (A) (directly or indirectly) contacting the fluid with an aqueous solution comprising at least one lower valence state polyvalent metal chelate of a

polyamino disuccinic acid and optionally additionally containing an absorbent for SO₂ and/or a sulfite.

The process optionally additionally comprises at least one of the
5 following steps:

- (B) thermally stripping sulfur dioxide from an SO₂-rich absorbent solution to obtain an SO₂-lean absorbent solution;
- (C) directing the absorbent solution to a cathode compartment in an
10 electrochemical cell, said cell having an anode in an anode compartment separated (preferably by a membrane) from a cathode in said cathode compartment, and imposing an electrical potential across said anode and said cathode to reduce oxidized chelates in said cathode compartment to obtain a regenerated absorbent solution;
- 15 (D) recycling said regenerated absorbent solution to contacting step (A);
(E) converting heat stable amine salts into free amine absorbent in said cathode compartment;
- (F) separating salt anions from said cathode compartment through said anionic exchange membrane into said anode compartment;
- 20 (G) circulating an aqueous electrolyte solution through said anode compartment;
- (H) periodically refreshing said electrolyte to eliminate byproduct salts in said anode compartment;
- (I) adjusting said regenerated absorbent solution to a pH of from 3 to 8 for a
25 recycling step;
- (J) (when HADS is formed) mixing at least a portion of hydroxylaminedisulfonate in a reaction zone in an aqueous environment of pH of 4.2 or less, thereby converting said hydroxylaminedisulfonate to ammonium ions and sulfate ions in a second aqueous solution;
- 30 (K) contacting said second aqueous solution with a second ammonium ion-absorbing sorbent suitable for removing ammonium ions from said second aqueous solution and separating said second sorbent from said second aqueous solution;
- (L) eluting said second sorbent and exposing the eluted ammonium ions or
35 ammonia to nitrogen oxides at a temperature sufficient to form nitrogen and water therefrom; and/or

(M) removing said sulfate ions from said second aqueous solution by forming a sulfate salt precipitate.

The following examples are offered to illustrate but not limit the invention. Percentages, ratios and parts are by weight unless stated otherwise. Examples of the invention (Ex.) are designated numerically, while comparative samples (C.S.), which are not examples of the invention, are designated alphabetically.

10 **EXAMPLE 1: PREPARATION OF ETHYLENEDIAMINEDISUCCINIC ACID FROM ETHYLENEDIAMINE AND MALEIC ACID AND PREPARATION OF THE FERRIC CHELATE**

A sample, 120.5 grams, of maleic acid (1.03 mole - Fisher reagent grade) was added to a beaker. Deionized water (120 grams) and 167 grams of 50 percent NaOH (2.08 mole - Fisher reagent grade) were added, and the mixture was stirred until dissolution was observed. The resulting solution was transferred to a 1 liter stainless steel autoclave vessel using 40 mL of deionized water as rinse. A sample, 31.03 grams, of ethylenediamine (0.51 mole - commercially available from The Dow Chemical Co.) was slowly added to the stirred (magnetic stirrer) sodium maleate solution over a 10 minute period. Then a cap was placed on the autoclave which was equipped with a thermowell and thermometer connected to a Therm-O-Watch™ temperature controller (commercially available from Instruments for Research & Industry (Cheltenham, Pa.)). Heat was supplied by a 30" x 0.75" (76.2 cm x 1.9 cm) section of heating tape wrapped around the autoclave which was then insulated with glass wool. Stirring was achieved by a magnetically-driven 1.5" (3.8 cm) Teflon™ polytetrafluoroethylene coated stirrer bar. Temperature was maintained at 140°C for 9 hours, after which the mixture was allowed to cool to room temperature. The carbon NMR and proton NMR of the reaction mixture indicated essentially no remaining ethylenediamine and a very small amount of residual maleic acid. The reaction mixture was adjusted to a pH of approximately 2.0 with 36-37 percent hydrochloric acid (commercially available from Aldrich Chemical Co.). A powdery white precipitate developed and was filtered with Whatman #41 filter paper in a Buchner funnel. The precipitated solid was washed twice with 300 mL of deionized water. The resulting solids

were dried overnight in a vacuum oven at 60°C. Approximately 108 grams of product were obtained (74 percent yield of acid). The carbon NMR and proton NMR indicated essentially pure ethylenediaminedisuccinic acid.

5 PREPARATION OF FERRIC-ETHYLENEDIAMINEDISUCCINIC ACID AND STABILITY AT VARIOUS pH's

An approximately 0.01 M iron (ferric) - ethylenediaminedisuccinic acid chelate solution was prepared by adding 1.63 grams of
10 ethylenediaminedisuccinic acid and 200 mL of deionized water to a beaker. The slurry was stirred with a magnetic stirrer bar, and the pH was adjusted to 10.0 with 1.43 grams of 50 percent NaOH solution. A sample, 2.4 grams, of iron nitrate solution (11.75 percent iron), commercially available from Shepherd Chemical Company, were added with stirring. The pH of the solution, which
15 drops to 1.7, was adjusted to 6.6 with aqueous ammonia (29 percent concentration) solution (commercially available from J. T. Baker Chemical Co.). The iron chelate solution was then diluted in a volumetric flask to a final volume of 500 mL. Fifty gram aliquots of the solution were then placed in four 2 oz. (0.059 l) bottles and the pH of each was adjusted to 7.0, 8.05, 9.1 and 10.0
20 respectively with a few drops of an aqueous ammonia solution. One 50 gram aliquot was adjusted to a pH of 6.0 with a few drops of dilute hydrochloric acid, and one 50 gram aliquot was adjusted to a pH of 10.5 with a 10 percent solution of sodium carbonate (8.5 g). The sample that was pH 10.5 develops an iron hydroxide precipitate almost immediately. The sample at pH 10.0
25 begins to form iron hydroxide after 4 hours. The samples that were pH 6.0, 7.0, 8.05, and 9.1 do not develop any noticeable iron hydroxide. The samples were allowed to stand for 6 days at which time the "overheads" (that is liquids not containing visible solids) from each of the samples were analyzed for soluble iron by inductively coupled plasma spectroscopy. Results are given in
30 Table 1.

Table 1
Fe(III) - EDDS vs pH

pH	ppm* Fe in solution	percent Fe in solution
6.0	669	100
7.0	671	100
8.05	671	100
9.1	674	100
10.0	235	35
10.5	74	10

* parts per million by weight

- 5 This data shows that EDDS can complex iron and keep it in a soluble form (and thus available for reaction) at the pH values that are used for the applications described in the invention (that is, photographic bleaching agents, hydrogen sulfide abatement, and other processes.)

10 **EXAMPLE 2: PREPARATION OF DIETHYLENETRIAMINE N,N'-DISUCCINIC ACID AND STABILITY AT VARIOUS pH's**

- 15 Diethylenetriamine disuccinic acid was prepared and isolated by the procedure of Example 1 except that 51.5 g of diethylenetriamine were used in place of ethylenediamine and 116.1 g of maleic acid were used. Also, 160.0 g of 50 percent sodium hydroxide solution were used. The ability to complex iron at various pH values was determined in the same manner as was described for EDDS in Example 1 with the results in Table 2.

TABLE 2

pH	ppm* Fe in solution	percent Fe in solution
5.9	531	99
7.0	526	98
8.0	535	100
9.2	527	99
10.0	531	99
10.5	166	31
11.0	22	4

*parts per million by weight

- 5 This data shows diethylenetriamine N,N"-disuccinic acid is an excellent chelating agent for iron and enables iron to remain soluble and available for reaction for the uses described in the invention.

10 **EXAMPLE 3: BIODEGRADABILITY SCREENING VIA ASTM D2667
SEMI-CONTINUOUS ACTIVATED SLUDGE TEST**

The procedure of ASTM D-2667-82 was used to determine the inherent biodegradability of EDDS.

- 15 Copper titration value was used to measure the extent of biodegradation of the chelating agents during the procedure. Titration was performed using ammonium purpurate (indicator for complexometric titration commercially available from Aldrich Chemical Co., Inc. under the trade designation Murexide) as the indicator at approximately pH 8, and using sodium acetate as
20 buffer. Titration of EDDS in 100 mL water with 0.01 molar copper chloride resulted in a 1:1 (molar) chelation of copper. Analyses were performed daily for a period of 28 days.

- 25 Using the above procedure, EDDS was found to be greater than 80 percent biodegradable in less than 28 days.

A control was used to verify the absence of interfering chelating substances in the test.

These results of the biodegradability test show that EDDS was inherently biodegradable and could be expected to be utilized by organisms in a municipal treatment facility after an acceptable acclimation period.

EXAMPLE 4: AND COMPARATIVE SAMPLES A : REDOX POTENTIALS FOR EDDS AND EDTA

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The Reduction Potential of ferric complexes were measured using normal pulse polarography with a saturated calomel reference electrode. Polarographic data was obtained on a Bioanalytical Systems BAS-100a Voltammetric Analyzer interfaced to a Metrohm VA 663 Multimode electrode stand according to the procedure described in Electrochemical Methods, Fundamentals and Applications by A. J. Bard and L. F. Faulkner, 1980, Wiley. Solutions were prepared of complexes of EDDS (Ex. 4) and EDTA (ethylenediaminetetraacetic acid) (as C.S. A), 0.001 molar in concentration in iron (III) [added as ferric perchlorate] and with a 10 mole percent excess of chelating agent. The solutions were 0.1 molar in NaClO_4 , and adjusted to pH 5 with NaOH and/or HClO_4 as needed to reach the stated pH, diluted with the same electrolyte solution. Perchlorate electrolyte was used because perchlorate was 'non-coordinating', that was it can not interact with the ferric center and interfere in the experiment.

25

Table 3

example/ sample	chelate	reduction potential
Ex. 4	Fe(EDDS)	-126 mV
C.S. A*	Fe(EDTA)	-135 mV

*not an example of the invention

30 The polarographic data shows that Fe(EDDS) gives a very good reversible reduction. The Fe(EDDS) was 10 millivolts easier to reduce than the commercially used Fe(EDTA). This indicates that the Fe(EDDS) complex will

oxidize silver in the photographic bleach process but was not sufficiently strong as an oxidizing agent to initiate bleach-fixer stability problems.

5 The data in Table 3 for EDDS represents an average of two slightly different potentials distinguishable at high resolution. Thus, there appeared to be two solution species in the Fe(EDDS) which were close in potential. These are believed to represent different isomers of the complex since ethylenediaminedisuccinic acid has two asymmetric carbons as discussed earlier. The different isomers of the polyamino disuccinic acids and their metal
10 complexes are within the scope of the invention.

EXAMPLE 5: H₂S ABATEMENT

A 2000 mL sample of 2 percent Fe (III) solution prepared from
15 ethylenediamine disuccinic acid and iron nitrate (pH adjusted to ~7 with aqueous ammonia) was placed in a four liter kettle equipped with a stirrer, thermometer, heating mantle, temperature controller, gas lines, caustic scrubber lines, pump, and sulfur filter, and allowed to equilibrate. The temperature was maintained at 120°C. A gas monitor was engaged and lead
20 acetate tape placed around the flask joints and gas fittings. Air at approximately 500 standard cubic feet per minute (scfm) (14,160 liters per minute) was sparged into the bottom of the flask through a 7 μ stainless steel frit using 1/4 (0.64 cm.) stainless steel tubing. Air sparging was done for 30
25 minutes to assure there was little ferrous iron present. After the sparging was completed, 100 scfm (2832 liters per minute) of a mixture of H₂S and N₂ gases were introduced for 10 minutes to the reaction mixture through the 7 μ sparge frit. After the addition of gas mixture, some sulfur particles were noted forming on the surface of the reaction mixture. No breakthrough of the H₂S
30 gas was determined at the 10 ppm level by the monitor and no darkening of the lead acetate paper was observed. The gas was shut off and the sulfur filtered from the solution.

This data shows that the ferric chelate of ethylenediamine disuccinic acid is effective in the abatement of hydrogen sulfide.

EXAMPLE 6: CHELATION OF COPPER WITH POLYAMINO DISUCCINIC ACIDS

Ethylenediamine disuccinic acid and diethylenetriamine disuccinic acid
5 were titrated with standard 0.01 M copper chloride solution. The titrations were
performed using ammonium purpurate (indicator for complexometric titration
commercially available from Aldrich Chemical Co., Inc. under the trade
designation Murexide) at a pH of approximately 8 using sodium acetate as
10 buffer. Both polyamino disuccinic acids complexed copper at a molar ratio of 1
mole of copper per mole of polyamino disuccinic acid.

EXAMPLE 7: COMPLEXATION OF COPPER IN ALKALINE SOLUTIONS

To be effective in an electroless copper plating bath, a chelating agent
15 must maintain the copper in a soluble form in the pH range of 10 to 14. An
especially preferred range is 11 to 12.5. To determine the effectiveness of the
polyamino disuccinic acids to prevent the precipitation of copper across this pH
range, a 0.05 M copper chelate solution of ethylenediamine disuccinic acid was
20 prepared from copper chloride, ethylenediamine disuccinic acid and sodium
hydroxide. Approximately 70.0 gram portions were adjusted with sodium
hydroxide solution to pH values of 10, 12, and 14. The ethylenediamine
disuccinic acid was observed to maintain the copper in solution at these pH
values preventing the precipitation of insoluble copper hydroxide. By
25 comparison, a 0.05 M copper solution prepared without the polyamino
disuccinic acid ligand, used in the same manner at a pH of 10, 12 and 14
resulted in precipitation of insoluble copper hydroxide from the solutions almost
immediately.

EXAMPLES 8 AND 9: DISSOLUTION OF IRON OXIDE SCALE

30 A sample, 1.0 gram, of ethylenediamine disuccinic acid (EDDS) was
dissolved in deionized water, and sufficient aqueous ammonia solution was
added to obtain a pH of 9.0. Deionized water was added to obtain a 5 weight
percent EDDS solution. The resulting solution was heated at 100°C for three
35 hours with 0.2 grams of iron oxide (Fe_3O_4) and cooled to room temperature.
The amount of soluble iron was then determined by inductively coupled plasma

spectroscopy. After 3 hours, approximately 31 weight percent of the iron oxide was dissolved. (Example 8)

5 In a similar experiment an EDDS solution was adjusted to a pH of 4.5 with an aqueous ammonia solution. After three hours at reflux, approximately 70 weight percent of the iron oxide had dissolved. (Example 9)

This data shows that ammoniated polyamino disuccinic acids are effective in dissolving iron oxide scales.

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EXAMPLE 10: PREPARATION OF ZINC CHELATE

15 The zinc chelate of ethylenediamine disuccinic acid was prepared by dissolving 0.0055 moles (1.64 g) of ethylenediamine disuccinic acid in 6.0 grams of deionized water and 3.2 grams of 25 percent NaOH (sodium hydroxide). A sample, 0.005 moles (0.68 g), of zinc chloride was added with stirring. The final pH was adjusted with 25 percent aqueous NaOH solution to a pH of 7.6 and deionized water was added to obtain a final solution containing 2.8 percent chelated zinc.

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EXAMPLE 11: PREPARATION OF MANGANESE CHELATE

25 The manganese chelate of ethylenediamine disuccinic acid was prepared by dissolving 0.0055 moles of ethylenediamine disuccinic acid in 5.8 grams of deionized water and 2.6 grams of 25 percent NaOH solution. A sample, 0.005 moles, of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1.0 g) was added with stirring. The pH was adjusted to 6.7 with 25 percent NaOH solution, and water was added to give a final solution containing 2.4 percent chelated manganese.

CLAIMS

1. A method of bleaching or bleach-fixing a photographic material which characterized in that said material is contacted with a bleaching solution containing a bleaching agent comprising a ferric complex of a polyamino disuccinic acid.

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2. The method of Claim 1 wherein the polyamino disuccinic acid has at least two nitrogens to each of which is attached a succinic acid or salt group and said polyamino disuccinic acid has from 10 to 50 carbon atoms which are unsubstituted or inertly substituted, and wherein the polyamino disuccinic acid has from 2 to 6 nitrogen atoms, said nitrogen atoms being separated by alkylene groups of from 2 to 12 carbon atoms each.

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3. The method of Claim 1 wherein the polyamino disuccinic acid has only two nitrogens to which succinic acid or salt groups are attached, which nitrogens are also bonded to at least one alkyl or alkylene group and have their remaining valence filled with hydrogen, alkyl or alkylene groups, and wherein the polyamino disuccinic acid the two nitrogens to which succinic acid or salt groups are attached are terminal, that is they have hydrogen as one substituent thereon.

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4. The method of Claim 1 wherein the polyamino disuccinic acid is selected from ethylenediamine N,N'-disuccinic acid, diethylenetriamine N,N'-disuccinic acid, triethylenetetraamine N,N''-disuccinic acid, 1,6-hexamethylenediamine N,N'-disuccinic acid, tetraethylenepentamine N,N'''-disuccinic acid, 2-hydroxypropylene-1,3-diamine N,N'-disuccinic acid, 1,2-propylenediamine N, N'-disuccinic acid, 1,3-propylenediamine N,N'-disuccinic acid, cis-cyclohexanediamine N,N'-disuccinic acid, trans-cyclohexanediamine N,N'-disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid and combinations thereof.

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5. The process of Claim 1 wherein the polyamino disuccinic acid is EDDS.

35

6. The method of any of Claims 1, 2, 3, 4, or 5 wherein the bleaching agent is present in an amount of from 0.05 to 1 mole per liter of solution, the complex has a molar ratio of polyamino disuccinic acid to ferric ion of from 1:1

to 5:1, and wherein the bleaching solution additionally contains a water-soluble halide.

5 7. Use of a polyamine disuccinic acid as a photographic bleaching or bleach-fixing agent.

8. An aqueous photographic bleaching solution characterized in that the bleaching agent is a ferric complex of a polyamino disuccinic acid.

10 9. A method of electroless deposition of copper upon a non-metallic surface receptive to the deposited copper characterized in that the non-metallic surface is contacted with an aqueous solution comprising a soluble copper salt and a polyamino disuccinic acid.

15 10. The method of Claim 20 wherein the solution has a pH of from 10 to 14 and additionally comprises a reducing agent.

20 11. In a process for plating copper on non-metallic surfaces, only selected portions of which have been pretreated for the reception of electroless copper, by immersing the surface in an autocatalytic alkaline aqueous solution comprising, in proportions capable of effecting electroless deposition of copper, a water soluble copper salt, a complexing agent for cupric ion, and a reducing agent for cupric ion, the improvement comprising using as the complexing agent for cupric ion, a polyamino disuccinic acid.

25 12. A bath for the electroless plating of copper characterized in that a complexing agent for cupric ions is a polyamino disuccinic acid.

30 13. A method for removing iron oxide deposits from a surface characterized in that the deposits are contacted with a solution comprising an ammoniated polyamino disuccinic acid.

14. A method for removing H_2S from a fluid by contacting said fluid with an aqueous solution at a pH suitable for removing H_2S characterized in that said solution contains at least one higher valence polyvalent metal chelate of a polyamino disuccinic acid.

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15. The process of Claim 26 wherein the metal is Fe^{+3} and the polyamino disuccinic acid is EDDS.

10 16. A method of removing NO_x from a fluid characterized in that the fluid is contacted with an aqueous solution of at least one lower valence state polyvalent metal chelate of a polyamino disuccinic acid.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05674

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : Please See Extra Sheet.

US CL : 430/393, 430, 461; 427/443.1; 106/1.23, 1.26; 134/2, 41, 42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/393, 430, 461; 427/443.1; 106/1.23, 1.26; 134/2, 41, 42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A, 0 532 003 (KONICA CORPORATION) 17 March 1993, pages 2, line 55 to page 5, line 56; page 6, lines 33-34.	1-6, 8
X	JP, A, 5-72695 (KONICA CORP) 26 March 1993, pages 1-5.	1-6, 8
X, E	US, A, 5,316,898 (UEDA ET AL) 31 May 1994, col. 3, lines 7-22; col. 7, line 7 to col. 8, line 28; col. 29, lines 20-36.	1-6, 8
X	SU, A, 1043137 (KOSTROMINA ET AL) 23 September 1983, Abstract and Derwent Abstract.	8

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be part of particular relevance
* E		earlier document published on or after the international filing date
* L		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* O		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* A	document member of the same patent family

Date of the actual completion of the international search

08 SEPTEMBER 1994

Date of mailing of the international search report

SEP 27 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

Charles Bowers, Jr.

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05674

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chemicke Zvesti, Volume 20, Number 6, pages 414-422, 1966, (MAJER et al.), "New Complexanes. VIII. Ethylenediamino-N,N'-disuccinic Acid and Investigations of its Heavy Metal Complexes by Spectrophotometry", especially table 3, page 420, and Chem. Abstr.	8, 12
A	US, A, 3,460,953 (SCHWARTZ) 12 August 1969.	9, 11, 12
A	SU, A, 1180404 (ELECTROTECH INST) 23 September 1985.	9, 11, 12
A	JP, A, 55-94468 (NIPPON ELECTRIC KK) 17 July 1980.	9, 11, 12
A	US, A, 5,002,078 (KAES) 26 March 1991.	13
A	Inorg. Chem., Volume 7, Number 11, pages 2405-2412, November 1968, (NEAL et al).	12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05674

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 7
because they relate to subject matter not required to be searched by this Authority, namely:

Claim 7 is directed to a "USE" which is not method terminology. "USE" claims are not searched by this International Searching Authority. PCT Article 17(a)(2)(i).
2. ☐ Claims Nos.: 10 and 15
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Claims 10 and 15 are depended from nonexistent claims, hence the limitations of the claims were unknown.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
1-6, 8, 9, 11-13
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05674

A. CLASSIFICATION OF SUBJECT MATTER: IPC (5):

G03C 7/00, 5/42, 5/44; B05D 1/18; B22F 7/00; C09D 5/00, 5/10; C23C 16/00, 18/00, 20/00; C03C 23/00; C23G 1/00, 1/02; B08B 3/14, 7/00

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

- I. Claims 1-6, 8, drawn to a method of bleaching or bleach-fixing a photographic material using a particular bleaching agent, and a composition for so doing, classified in class 430, subclass 393.
- II. Claims 9, 11, 12, drawn to a method of electroless deposition of copper and a composition for so doing, classified in class 427, subclass 443.1.
- III. Claim 13, drawn to a method for removing iron oxide deposits using a particular solution, classified in class 134, subclass 2.
- IV. Claim 14, drawn to a method of removing hydrogen sulfide from fluids using a particular agent, classified in class 423, subclass 228.
- V. Claim 16, drawn to a method of removing nitrogen oxides from fluids using a particular agent, classified in class 423, subclass 235.

The listed inventions lack unity of invention under PCT Rules 13.1 to 13.3 because, although there is a common element of the particular ligand used in the compositions which are used in the various processes of each separate invention, the processes themselves are radically different.